https://ntrs.nasa.gov/search.jsp?R=20160012489 2019-08-29T17:34:25+00:00Z

Alternative to Nitric Acid Passivation

NASA Corrosion Technology Laboratory (CTL)
&
NASA Technology Evaluation for Environmental Risk Mitigation (TEERM)

2016 INTERNATIONAL WORKSHOP ON ENVIRONMENT AND ALTERNATIVE ENERGY
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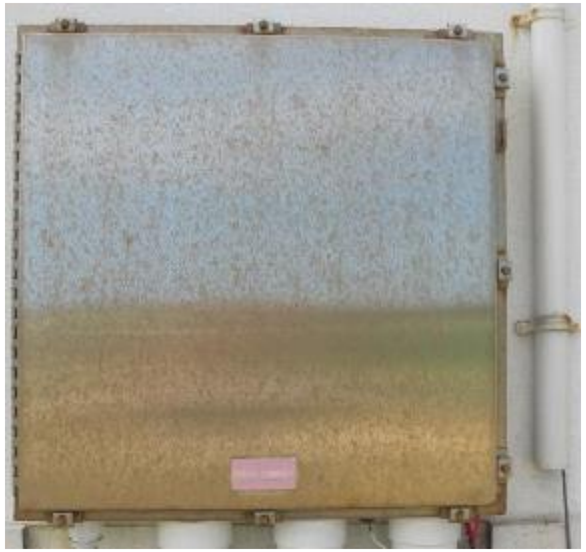
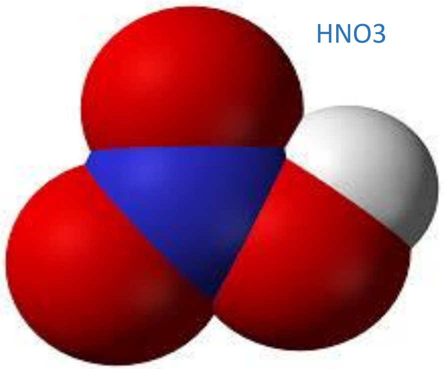
Background

- Corrosion is an extensive problem that affects the National Aeronautics and Space Administration (NASA) and European Space Agency (ESA).
- The deleterious effects of corrosion result in steep costs, asset downtime affecting mission readiness, and safety risks to personnel.
- It is vital to reduce corrosion costs and risks in a sustainable manner.



Risk

- Nitric acid passivation results in fumes that contain nitrogen dioxide and nitrogen oxide (NOx) emissions which are considered greenhouse gases; Best Available Technology (BAT) to be employed to control nitric acid and NOx emissions
- Nitric acid passivation requires 25% or 50% concentration of the strong acid.
- Wastewater generated from the passivation process is regulated under the U.S. Environmental Protections Agency's (EPA) Metal Finishing Categorical Standards
- Nitric acid can remove beneficial heavy metals (nickel, chromium, etc.) that give stainless steel its desirable properties.



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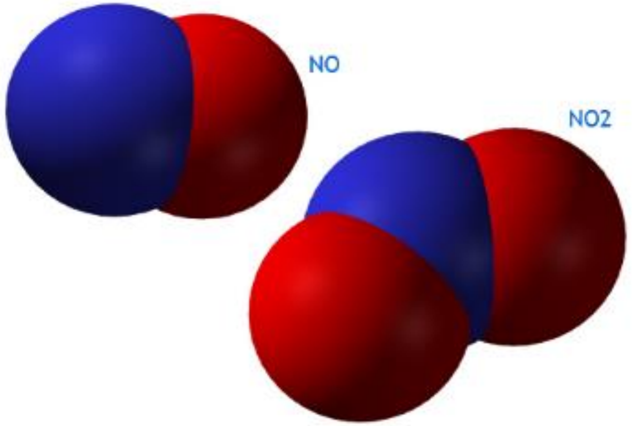

http://www.offshoreenergytoday.com


http://www.theguardian.com

Specification

- Citric acid passivation is allowed per:
  - ASTM A 967 (*Standard Specification for Chemical Passivation Treatments for Stainless Steel Parts*)
  - AMS 2700 (*Passivation Treatments for Corrosion-resistant Steel*)
- Citric acid passivation is not a new technology; it was developed (many years ago) for the beverage industry in Germany to process containers that were free of iron which causes an unwanted taste to the beverage.
- While citric acid use has become more prominent in industry in the U.S., there is little evidence that citric acid is a technically sound passivating agent, especially for the unique and critical applications encountered by NASA and ESA.


https://www.agra-net.net


http://www.dowlandbach.com

Benefits of Citric Acid Passivation

- Citric acid is a bio-based material that helps government agencies meet the procurement requirements of the Farm Security and Rural Investment Act of 2002
- There are no toxic fumes created during the citric acid passivation process making it safer for workers.
- Nitric acid passivation requires 25% or 50% concentrations of the strong acid which are extremely corrosive and hazardous to workers.
- Citric acid removes iron from the surface more efficiently than nitric acid and therefore uses much lower concentrations reducing material costs.
- Citric acid-based processing baths retain their potency for longer periods requiring less frequent refilling and reduced volume and potential toxicity of effluent and rinse water.

http://vegnews.com

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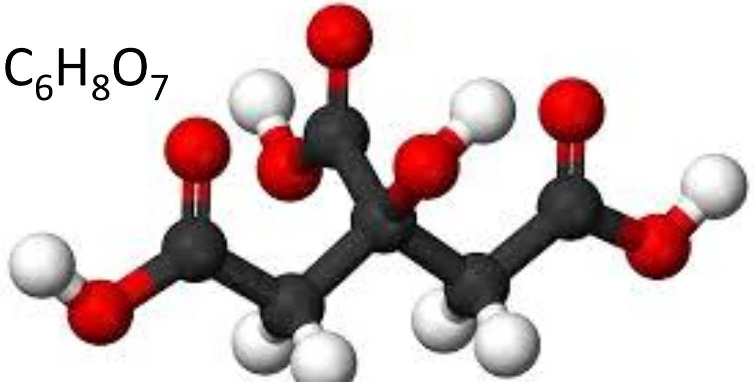

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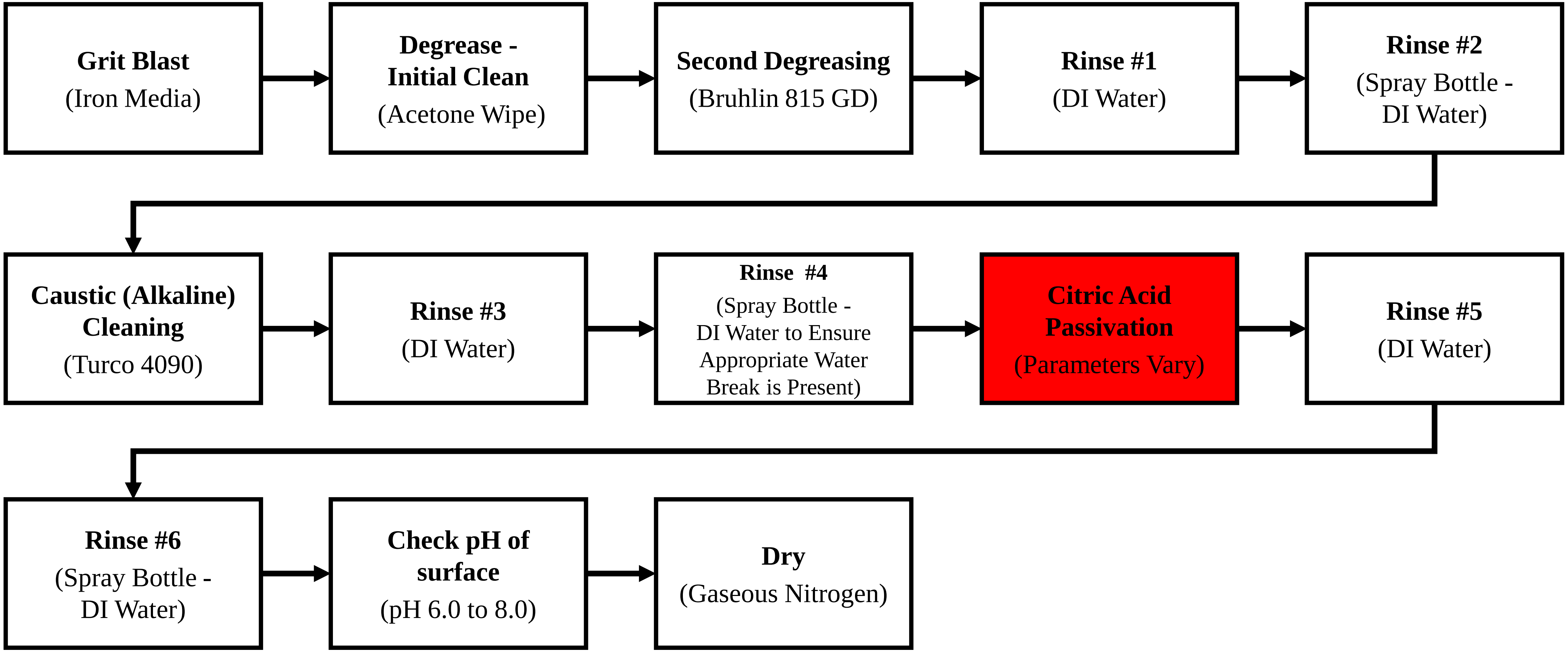
Objective

- The primary objective of this effort is to qualify citric acid as an environmentally-preferable alternative to nitric acid for passivation of stainless steel alloys.

Test Specimen Preparation

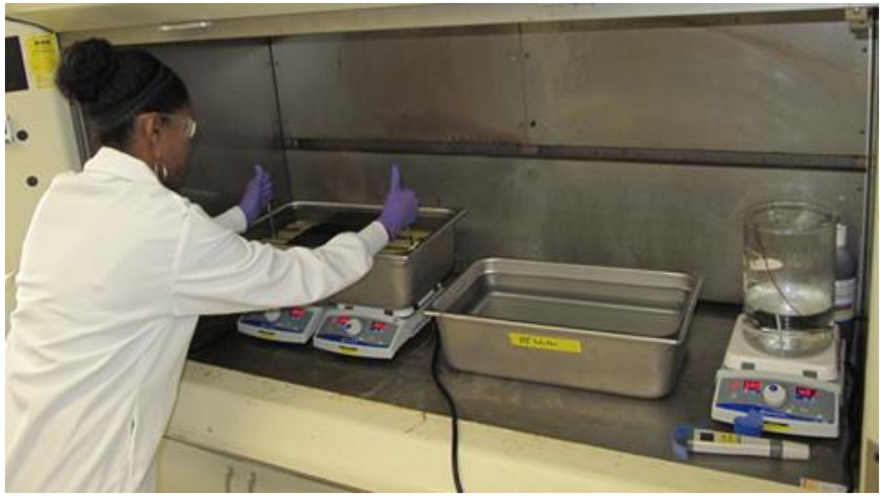
The NASA Corrosion Technology Lab followed the United Space Alliance (USA) procedure for passivation:



Parameter Optimization

Test panels of each stainless steel alloy were prepared using various process parameters

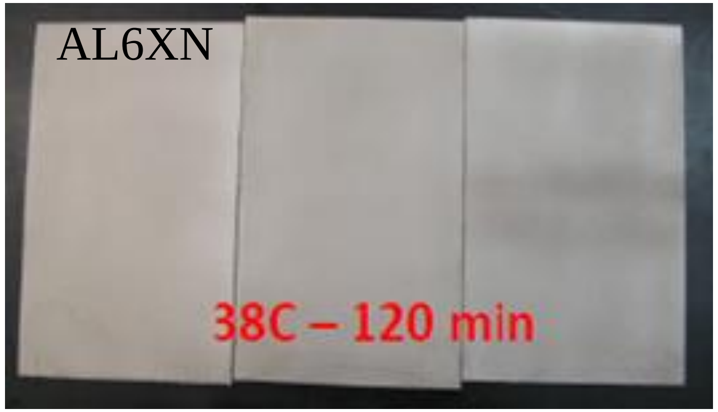
- Citric Acid Concentration: 4% ONLY in this phase
- Immersion Times: 60, 90, and 120 minutes
- Bath Temperatures: 38°C (100°F), 60°C (140°F), and 82°C (180°F)
- Salt Spray Testing per ASTM B 117
- Corrosion Resistance Evaluation every 168 hours up to 504 hours of salt spray testing
- Parameters resulting in the best corrosion resistance shall be used for preparation of that substrate’s test panels for the remainder of the testing



Process Parameters Used for Testing				
Alloy	Passivation	Concentration (%)	Bath Temperature (°C)	Dwell Time (minutes)
AL6XN	Nitric Acid	22.5	60	20
	Citric Acid	4	38	120
A286	Nitric Acid	50	64	30
	Citric Acid	4	82	60
304	Nitric Acid	22.5	60	20
	Citric Acid	4	49	120
17-4PH[1]	Nitric Acid	50	64	30
	Citric Acid	4	38	30
316	Nitric Acid	22.5	60	20
	Citric Acid	4	60	90
321	Nitric Acid	22.5	60	20
	Citric Acid	4	82	60
410	Nitric Acid	50	64	30
	Citric Acid	4	82	60
440C	Nitric Acid	50	64	30
	Citric Acid	4	60	60
15-5PH	Nitric Acid	50	64	30
	Citric Acid	4	82	60
17-7 PH	Nitric Acid	50	64	30
	Citric Acid	4	82	60

Note 1 = Citric acid parameters were initially determined by USA

All other citric acid parameters were determined by KSC Corrosion Lab



@ 504 Hours of ASTM B117 Exposure

@ 504 Hours of ASTM B117 Exposure

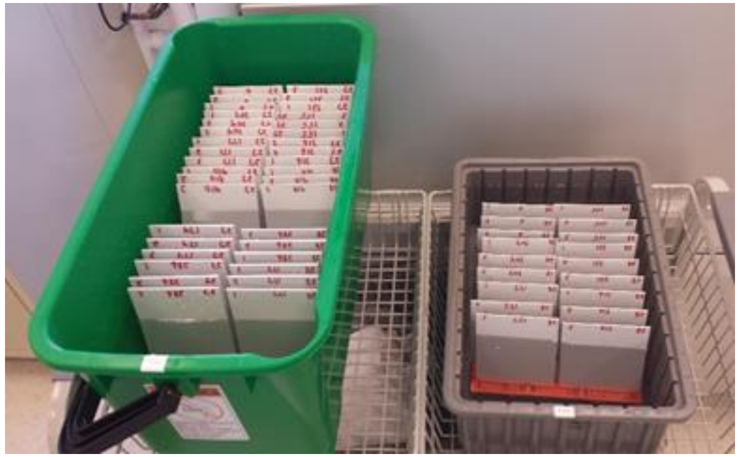
Testing

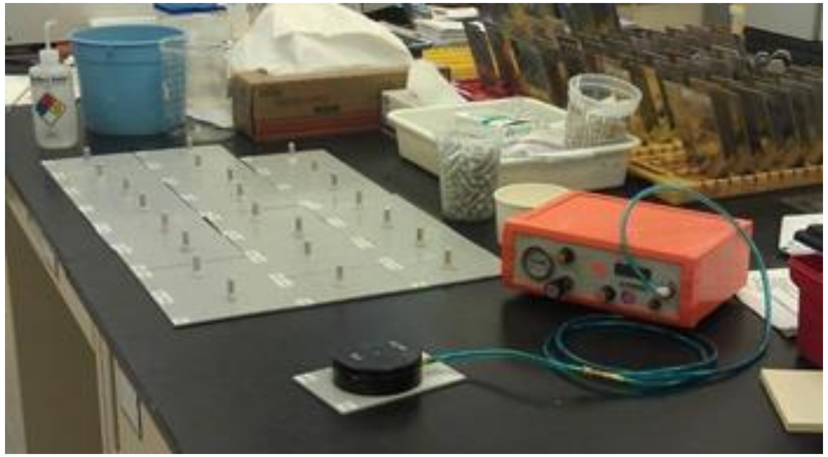
Test	Test Methodology References	Acceptance Criteria	Location
X-Cut Adhesion by Wet Tape	ASTM D 3359	Alternative performs as well or better than control process	NASA Corrosion Technology Lab
Tensile (Pull-off) Adhesion	ASTM D 4541		
Cyclic Corrosion Resistance	GMW 14872		
Atmospheric Exposure Testing	ASTM D 610		NASA Corrosion Technology Lab Atmospheric Exposure Site
	ASTM D 714		
	NASA-STD-5008		
Stress Corrosion Cracking	ASTM B 117		NASA Corrosion Technology Lab
	ASTM E 4		
	ASTM E 8		
	ASTM G 38		
	ASTM G 39		
	ASTM G 44 MSFC-STD-3029		
Fatigue*	ASTM E 466		
Hydrogen Embrittlement**	ASTM F 519		
* = Only one alloy was tested; 17-4PH			
** = Test specimens were made of AISI 4340 alloy steel, this is considered worst case			

Overall Test Results

4% Citric Acid

Test	Citric Acid Performance
X-Cut Adhesion by Wet Tape	Performs as well or better than control process for all alloys
Tensile (Pull-off) Adhesion	Performs as well or better than control process for all alloys
Cyclic Corrosion Resistance	Performs as well or better than control process for all alloys
Atmospheric Exposure Testing[1]	Performs as well or better than control process for the majority of alloys
Stress Corrosion Cracking	Performs as well or better than control process for all alloys
Fatigue[2]	Performs as well or better than control process for all alloys
Hydrogen Embrittlement[3]	Performs as well or better than control process for all alloys
1 = 17-4PH panels processed through the control process performed slightly better	
2 = Only one alloy was tested; 17-4PH	
3 = Test specimens were made of AISI 4340 alloy steel, this is considered worst case	

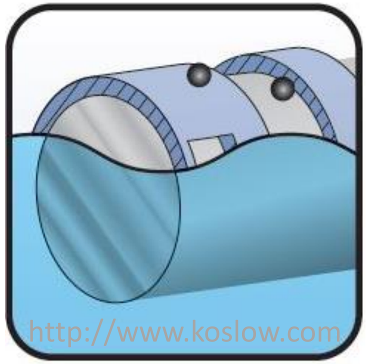




Expanded Scope to Evaluate 7% and 10% Citric Acid Concentration

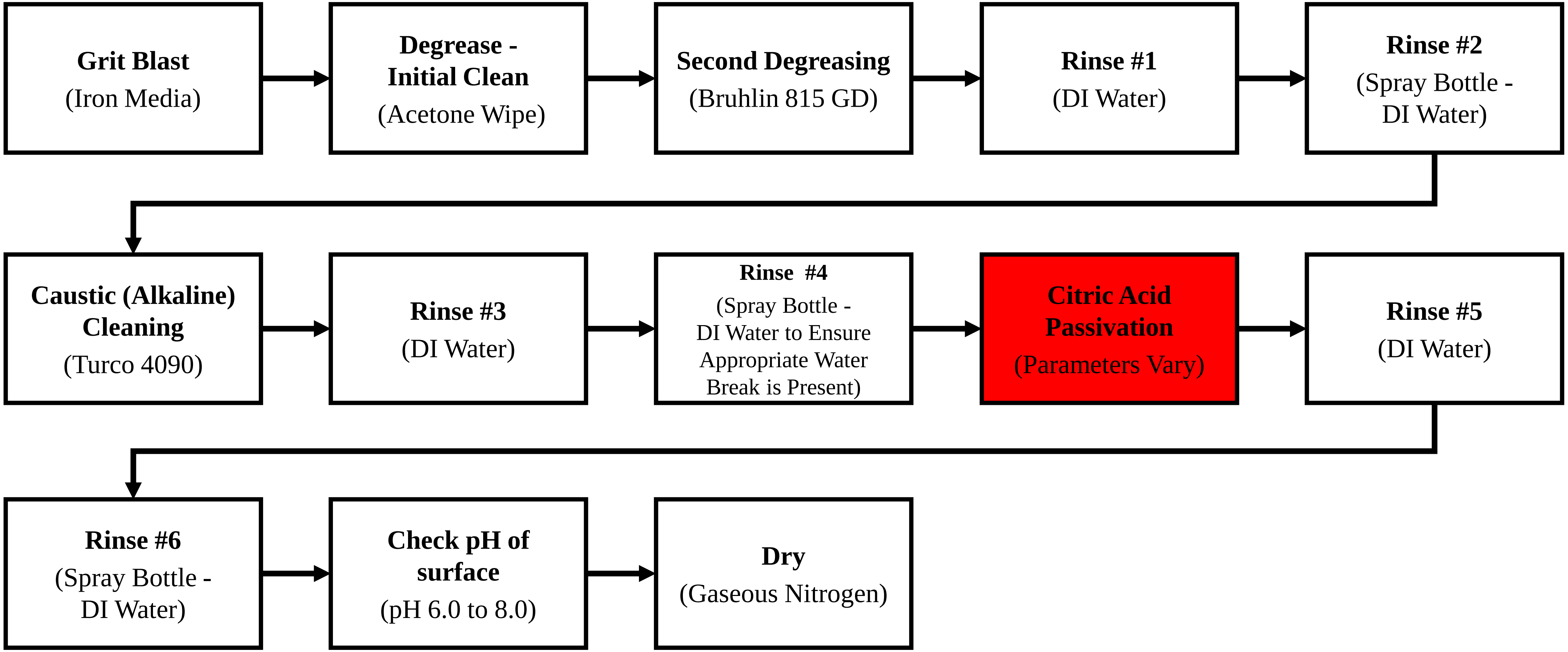
Alloy	Passivation	Concentration (%)			Bath Temperature (^{o}C)			Dwell Time (minutes)		
304	Citric Acid	4	7	10	38	60	82	60	90	120
316		4*	7	10	38	60	82	60	90	120
321		4*	7	10	38	60	82	60	90	120
13-8PH		4	7	10	38	60	82	60	90	120
15-5PH		4*	7	10	38	60	82	60	90	120
17-4PH		4	7	10	38	60	82	60	90	120
17-7PH		4*	7	10	38	60	82	60	90	120
A286		4	7	10	38	60	82	60	90	120
AL6XN		4	7	10	38	60	82	60	90	120

* Optimization testing completed in a previous project



Test Specimen Preparation

The NASA Corrosion Technology Lab followed the United Space Alliance (USA) procedure for passivation:



Parameter Optimization

Test panels of each stainless steel alloy were prepared using various process parameters

- Citric Acid Concentration: 4% (limited alloys), 7% and 10%
- Immersion Times: 60, 90, and 120 minutes
- Bath Temperatures: 38°C (100°F), 60°C (140°F), and 82°C (180°F)
- Salt Spray Testing per ASTM B 117
- Corrosion Resistance Evaluation after 2 hours of salt spray testing
    - SAE AMS 2700 & ASTM A967 = No signs of red rust or staining associated with free iron particles shall be observed
- Salt Spray Testing continued for an additional 166 hours

Salt Spray Results

- 168 hours of exposure
- 3 panels were tested per parameter set
- RED = 1 or more panels showed evidence of rusting
- GREEN = all 3 panels showed no signs of rusting

Alloy	Passivation	Concentration	Bath Temperature	Dwell Time (minutes) 60	90	120
304	Citric Acid	4%	38	RED	RED	RED
			60	GREEN	GREEN	GREEN
			82	GREEN	GREEN	GREEN
		7%	38	RED	GREEN	GREEN
			60	GREEN	GREEN	GREEN
			82	GREEN	GREEN	GREEN
		10%	38	RED	GREEN	GREEN
			60	GREEN	GREEN	GREEN
			82	GREEN	GREEN	GREEN
316	Citric Acid	4%*				
		7%	38	RED	RED	RED
			60	GREEN	GREEN	GREEN
			82	GREEN	GREEN	GREEN
		10%	38	RED	GREEN	GREEN
			60	GREEN	GREEN	GREEN
			82	GREEN	GREEN	GREEN
321	Citric Acid	4%*				
		7%	38	RED	GREEN	GREEN
			60	GREEN	GREEN	GREEN
			82	GREEN	GREEN	GREEN
		10%	38	GREEN	GREEN	GREEN
			60	GREEN	GREEN	GREEN
			82	GREEN	GREEN	GREEN
13-8PH	Citric Acid	4%	38	RED	RED	RED
			60	GREEN	GREEN	GREEN
			82	GREEN	GREEN	GREEN
		7%	38	RED	RED	RED
			60	GREEN	RED	GREEN
			82	GREEN	GREEN	GREEN
		10%	38	RED	RED	GREEN
			60	GREEN	GREEN	GREEN
			82	GREEN	GREEN	GREEN
15-5PH	Citric Acid	4%*				
		7%	38	RED	RED	RED
			60	GREEN	GREEN	GREEN
			82	GREEN	GREEN	GREEN
		10%	38	GREEN	GREEN	GREEN
			60	GREEN	GREEN	RED
			82	GREEN	GREEN	GREEN

Alloy	Passivation	Concentration	Bath Temperature	Dwell Time (minutes) 60	90	120
17-4PH	Citric Acid	4%	38	RED	RED	RED
			60	GREEN	GREEN	RED
			82	GREEN	GREEN	GREEN
		7%	38	RED	GREEN	RED
			60	GREEN	GREEN	GREEN
			82	GREEN	GREEN	GREEN
		10%	38	RED	GREEN	GREEN
			60	GREEN	GREEN	GREEN
			82	GREEN	GREEN	GREEN
17-7PH	Citric Acid	4%*				
		7%	38	RED	RED	RED
			60	GREEN	GREEN	GREEN
			82	GREEN	GREEN	GREEN
		10%	38	RED	RED	GREEN
			60	GREEN	GREEN	GREEN
			82	GREEN	GREEN	GREEN
A286	Citric Acid	4%	38	GREEN	GREEN	GREEN
			60	GREEN	GREEN	GREEN
			82	GREEN	GREEN	GREEN
		7%	38	RED	GREEN	GREEN
			60	GREEN	GREEN	GREEN
			82	GREEN	GREEN	GREEN
		10%	38	RED	GREEN	GREEN
			60	GREEN	GREEN	GREEN
			82	GREEN	GREEN	GREEN
AL6XN	Citric Acid	4%	38	RED	GREEN	GREEN
			60	GREEN	GREEN	GREEN
			82	GREEN	GREEN	GREEN
		7%	38	RED	RED	RED
			60	GREEN	GREEN	GREEN
			82	GREEN	GREEN	GREEN
		10%	38	RED	RED	GREEN
			60	GREEN	GREEN	GREEN
			82	GREEN	GREEN	GREEN

* Optimization testing completed in a previous project

Conclusions

- Regardless of alloy, higher citric acid concentrations, temperatures, and bath dwell times yielded the best results
- There is clear evidence that 38°C (100°F) had a significantly greater number of failures than either 60°C (140°F) or 82°C (180°F)
- When differentiating between 60°C and 82°C, there is not enough proof to signify that 82°C is better than 60°C because there is only a 1 percent difference in the failure data
- Increasing temperature increased difficulty in panel processing
- When scaled to an industrial process, the 82°C baths would require constant replenishing.
- Longer immersion times showed a positive trend in pass rates; 120 minutes may be the optimal immersion time.

Next Phase – Validation Testing

Test	Corrosion Protection	Requirement	Test Methodology	Evaluation	Acceptance Criteria
Salt Spray	Passivation Only	SAE AMS 2700	ASTM B 117	ASTM D 610	Alternative performs as well or better than control process
	Passivation + Primer & Topcoat	NASA-STD-5008	ASTM B 117	ASTM D 1654	
Tensile (Pull-off) Adhesion	Passivation + Primer	NASA-STD-5008	ASTM D 4541	ASTM D 4541	
Atmospheric Exposure Testing	Passivation Only	NASA-STD-5008	ASTM D 1014	ASTM D 610	
	Passivation + Primer & Topcoat			ASTM D 1654	

Questions?

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